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(54)【発明の名称】　鉛蓄電池用セパレータ並びにその製造法

(57)【特許請求の範囲】

【請求項１】合成樹脂製微多孔性シートの内外面に、酸化防止剤とリン酸系過酸化物分解剤とを含有するパラフィン系オイルを付着せしめて成る鉛蓄電池用セパレータ。

【請求項２】該パラフィン系オイルは、0.5%以上の酸化防止剤と0.5%以上のリン酸系過酸化物分解剤を含有して成る請求項１に記載の鉛蓄電池用セパレータ。

【請求項３】該パラフィン系オイルに含有する酸化防止剤とリン酸系過酸化物分解剤との合計量が５％を越えないようにして成る請求項２に記載の鉛蓄電池用セパレータ。

【請求項４】ポリオレフィン系樹脂に、無機粉体及び有機可塑剤を混合しシート状に溶融成型した後、有機可塑剤の一部又は全部を有機溶剤で抽出して微多孔性シートを形成した後、該微多孔性シートに酸化防止剤とリン酸系過酸化物分解剤を含有せしめたパラフィン系オイルをその微多孔性シートの内外面に付着させたことを特徴とする鉛蓄電池用セパレータの製造法。

【発明の詳細な説明】

〔産業上の利用分野〕

本発明は、鉛蓄電池用セパレータ並びにその製造法に関する。

〔従来の技術〕

従来、ポリエチレンセパレータは公知である。その製造法は、高密度ポリエチレン樹脂に無機粉体及び有機性可塑剤を混合し、シート状に溶融成型した後、有機溶剤で可塑剤の一部又は全部を抽出して微多孔性とすることにより製造されて居り、従来からポリエチレンセパレータは、耐酸化性に優れたものとされている。

〔発明が解決しようとする課題〕

然し乍ら、該ポリエチレンセパレータは、電動車用や自動車用の鉛蓄電池に組み込み使用される時は、最近、電池の使用が頻繁となり高温使用条件となった為、セパレータの使用環境が苛酷となり、かゝる使用条件では、該セパレータはこれと接する陽極板より発生する発生期の酸素や二酸化鉛の酸化作用により酸化劣化し、その酸化作用は、温度が高ければ高いほど活発である。従って、該セパレータは、かゝる高温下の苛酷な使用環境下では意外に早く酸化劣化し使用寿命が短縮される。一方、鉛蓄電池の陽極板の活物質は、かゝる高温においては、軟化脱落を生じ易く、電池の使用寿命の短縮をもたらす。

上記従来の欠点である高温下でのセパレータの酸化による寿命の短縮を防止するため、そのセパレータの表面にパラフィン系オイルを表面保護剤として含浸させることが行われているが、これだけでは充分な酸化劣化防止効果が得られていない。

更に、パラフィン系オイル中に、フェノール系酸化防止剤を混入したものをセパレータに含浸してみた所、セパレータの高温環境下での酸化劣化防止効果は或る程度認められたが、陽極活物質の接触による酸化劣化は防止できないと共に陽極活物質の軟化脱落を回避できず、従って、電池寿命の短縮は不可避であった。

〔課題を解決するための手段〕

本発明は、上記従来の不都合を解消し、耐高温酸化性の向上した而も鉛蓄電池の陽極活物質の高温軟化脱落防止機能を備えた鉛蓄電池用セパレータを提供するもので、合成樹脂製微多孔性シートの内外面に、酸化防止剤とリン酸系過酸化物分解剤とを含有するパラフィン系オイルを付着せしめて成る。

更に、本発明は、上記本発明の酸化防止剤とリン酸系過酸化物分解剤の両剤を含有する鉛蓄電池用セパレータを確実に製造し得る鉛蓄電池用セパレータの製造法を提供するもので、ポリオレフィン系樹脂に、無機粉体及び有機可塑剤を混合しシート状に溶融成型した後、有機可塑剤の一部又は全部を有機溶剤で抽出して微多孔性シートを形成した後、該微多孔性シートに酸化防止剤とリン酸系過酸化物分解剤を含有せしめたパラフィン系オイルをその微多孔性シートの内外面に付着させたことを特徴とする。

〔作 用〕

本発明の鉛蓄電池用セパレータは、そのシートの微孔内面並びにそのシート外面は、酸化防止剤とリン酸系過酸化物分解剤を含有するパラフィン系オイルで被覆されているので、電池内において、陽極板の活物質、即ち、過酸化物に対しそのオイル自体がセパレーターシート面との接触を防止し、同時にその含有する酸化防止剤とリン酸系過酸化物の相剰効果によって、セパレータシートの高温における酸化並びに連鎖的酸化を良好に防止し、セパレータシートの高温酸化劣化消耗を防止されるばかりでなく、特に、そのリン酸系過酸化物分解剤により陽極活物質、即ち、二酸化鉛の軟化、即ち、結晶の微細化、これに伴う活物質の脱落を積極的に防止でき、従って、電池寿命を著しく延長できる。

この場合、パラフィン系オイル中に含有する酸化防止剤は該オイルに対し0.5%以上、リン酸系過酸化物分解剤も0.5%以上を含有することが望ましく、その両者の合計量が５%を越えないように限定することが自己放電の防止上特に好ましい。このような比較的多量の両剤を含有するオイルを確実に微多孔性シートの内外面に付着せしめたセパレータを製造するには、前記の製造法に記載のように、成形シートを有機溶剤で有機可塑剤の一部又は全部を除去して微多孔性シートとした後に、該シートに該両剤を所望量含有せしめたパラフィン系オイル付着させることにより達成される。

〔実施例〕

次に、本発明実施例につき説明する。

本発明セパレータは、合成樹脂製微多孔性シートを主体とするが、その合成樹脂は一般に、耐酸化性が良いとされるポリオレフィン系樹脂、代表的には、ポリエチレン、就中、高密度ポリエチレンが比較的硬質で肉薄強靭なセパレータシートを得るに好ましい。これを溶融成形し、微多孔性シートとするには、例えば、これにDOPなどの有機性可塑剤に珪酸微粉体などの耐酸化性無機粉体とを適当な割合で混合し、加熱溶融したものを押し出し成形などによりシート状に成形した後、これに公知の任意の有機溶剤でその可塑剤の一部又は全部を抽出させて、その後に微多孔の形成された高密度ポリエチレンシートを作製する。本発明は、かゝる微多孔性シートの微多孔内面及びシートの外面に、酸化防止剤とリン酸系過酸化物分解剤とを含有せしめたパラフィン系オイルを付着させて成る鉛蓄電池用セパレータを構成することを特徴とするが、その製造法としては、前記の微多孔性シートを作製後、これを前記の両剤含有のパラフィン系オイル中に所望時間浸漬し、或いはこれを該シートの外面から噴霧器により均一にその所定量を吹き付けたり、或いは塗付ロールにより塗着させる等によって、その微多孔性シート内に均一に含浸せしめる。この場合、前記の両剤含有のパラフィン系オイルを適当な溶剤で適当な温度に希釈し、該微多孔性シートに含浸せしめた後、比較的低温で該溶剤を乾燥させて所定量の該オイルを付着せしめ本発明のセパレータを製造することができる。

而して、かゝる本発明のセパレータを常法に従って、鉛蓄電池の組み立てに当たり、その陰陽極板間に介在させて極板群としたものを電槽内に収容することにより下記に明らかにするように耐高温酸化性で長寿命の鉛蓄電池を提供することができる。

尚、上記の微多孔性ポリエチレンシートを作製するに当たり、その製造過程において、ポリエチレンがその加

熱溶融成形時に熱酸化劣化することを防止するため、その配合原料中に酸化防止剤を添加しておくことが好ましい。然し乍ら、該酸化防止剤は、爾後の有機溶剤による可塑剤の抽出工程で溶出されてしまい、得られる微多孔性シート中には、その痕跡量が残存する程度であるので、これをこのまゝ鉛蓄電池用セパレータとして使用した場合、陽極板よりの発生期の酸素や二酸化鉛によりその表面の酸化並びにその内部への連鎖的酸化が不可避であり、酸化消耗してその厚さが薄くなり所々に亀裂が生じたり、貫通孔を生ずるなどの酸化劣化をもたらし、鉛蓄電池は内部短絡現象を起こし寿命が尽きる。特に、電池内の温度が高温な繰り返しとなる様な使用条件では、更に酸化劣化は促進し、電池の短寿命をもたらす。そこで、そのセパレータに酸化防止作用のあるパラフィン系オイルを付着させたり、酸化防止剤のみを含有させたパラフィン系オイルを付着させたりしてその酸化防止を試みた。その結果、ある程度のセパレータの酸化防止効果は得られたが、陽極板の活物質の軟化脱落を生じ、又その活物質にセパレータが接触酸化することは避けられず、結局、電池に短寿命をもたらした。本発明によれば、種々検討の結果、酸化防止剤と、特にリン酸系過酸化物分解剤との併存により、鉛蓄電池が高温に晒されてもセパレータの酸化防止効果に加え、陽極板の活物質の軟化脱落が少なくなり、これによって電池の寿命延長、具体的には高温でのSAE寿命の増大をもたらすことを知見した。

本発明において、酸化防止剤としては従来から使用さている全ての種類のものが使用できるが、2,2′－メチレンビス（4－メチル－6－t－ブチルフェノール）、4,4′－ブチリデンビス（3－メチル－6－t－ブチルフェノール）、4,4′－チオビス（3－メチル－6－t－ブチルフェノール）など電池に無害なフェノール系の酸化防止剤を用いることが好ましい。

又、本発明による過酸化物分解剤は、特にTNPの如きリン酸系のものでなければならず、チオサルファイド系の如き非リン酸系過酸化物分解剤では、活物質の軟化、脱落防止ができないことが分った。

次に、本発明の特徴を下記の比較試験を通して明らかにする。

高密度ポリエチレン（重量平均分子量約20万）を主体とし、これに珪酸微粉体と有機性可塑剤としてパラフィン系オイルとを該ポリエチレンに対し夫々100重量%及び400重量%を配合し、その加熱溶融混合物を押し出し成形機により、厚さ0.5mmのシートに成形し、その成形シートを例えば、有機溶剤中を通過させて有機性可塑剤の一部又は全部を抽出後、加熱乾燥して微多孔性シートを得た。別個に、下記表1に示すように、酸化防止剤とリン酸系過酸化物分解剤との配合比を色々と変えて含有させた夫々のパラフィン系オイル、酸化防止剤と非リン酸系過酸化物分解剤とを含有させたパラフィン系オイルを調製したものを前記の微多孔性シートに、該シート重量に対し前記の各オイルを10%と20%付着させたものを作製した。更に、比較のため、微多孔性シートにパラフィン系オイルだけを20%付着させた微多孔性シートを作製した。

表　1

セパレータサンプルNo.	パラフィン系オイル中の含有量			オイル付着量
	酸化防止剤	過酸化物分解剤		
		リン酸系 (%)	非リン酸系 (%)	
	(%)			(%)
1	0.1	0.1	－	20
2A	0.5	0.5	－	10
2B	0.5	0.5	－	20
3A	1.0	1.0	－	10
3B	1.0	1.0	－	20
4A	1.0	4.0	－	10
4B	1.0	4.0	－	20
5	2.0	1.0	－	20
6	3.0	1.0	－	20
7	4.0	1.0	－	20
8	5.0	－	－	20
9	－	4.0	－	20
10	－	－	4.0	20
11	1.0	－	4.0	20
12	－	－	－	－

上記のサンプルNo.1～No.12の各鉛蓄電池用セパレータを使用し、夫々の鉛蓄電池用陰極板と陽極板と積層して極板群を組み、夫々の自動車用鉛蓄電池を作り、その夫々のセパレータの対応する試験電池サンプルNo.1′～No.12′の5時間率容量、C.C.A.、過充電寿命、65℃SAE寿命につき夫々試験した。その測定結果を下記表2に示す。

表　2

鉛蓄電池サンプルNo.	5時間率容量 (Ah)	C.C.A (A)	過充電寿命 (回数)	65℃SAE寿命 (回数)
1′	28.5	293	4	2500
2′A	28.5	294	6	2900
2′B	28.5	293	6	3000
3′A	28.5	292	8	3250
3′B	28.3	295	8	3500
4′A	28.3	290	8	3300
4′B	28.5	295	8	3400

鉛蓄電池サンプルNo	5時間率容量 (Ah)	C.C.A (A)	過充電寿命 (回数)	65℃SAE寿命 (回数)
5′	28.5	295	6	2950
6′	28.5	294	6	2900
7′	28.5	294	6	2900
8′	28.4	293	5	2550
9′	28.4	294	5	3000
10′	28.5	294	5	2500
11′	28.5	294	6	2500
12′	28.5	294	4	2400

上記の表１及び表２から明らかなように、セパレータシートに酸化防止剤とリン酸系過酸化物分解剤を付着させた本発明のセパレータNo.2A…No.7を使用した試験電池No.2A′…No.7′は、従来のセパレータNo.1′及びNo.12′に比し、過充電寿命及び65℃SAE寿命共に著しい延長効果が認められた。又、対比試験である酸化防止剤のみを含有したオイルを付着せしめたセパレータNo.8を使用した電池No.8では、表２に見られるように、これら両寿命の延長効果は認められず、又、リン酸系過酸化物分解剤のみを含有したオイルを付着せしめたセパレータNo.9を使用した電池No.8′では、同表に見られるように、SAE寿命の改善は見られたが、過充電寿命の延長効果は殆ど認められず、これに加え、試験終了後の当該電池を分解し、そのセパレータを点検した所、セパレータは酸化劣化を受けており、そのシートの厚さは薄くなり、その所々に亀裂が認められた。又、非リン酸系過酸化物分解剤の効果を検べるため、これのみを含有したオイルを付着せしめたセパレータNo.10及びこれと酸化防止剤の併用効果を検べるため、これらを含有したオイルを付着せしめたセパレータNo.11を夫々使用した電池No.

11′では、同表に見られるように、SAE寿命の延長効果が全く認められなかった。その上、これら電池No.10及びNo.10′及びNo.11′のセパレータの酸化劣化が前記のサンプルNo.8（No.8′）の場合と同様に認められた。

表には示さなかったが、これら全てのセパレータサンプル及び試験電池について、これらセパレータと接触していた陽極板について活物質の軟化、脱落の有無を点検した所、従来のセパレータNo.1及びNo.12及び比較セパレータNo.8〜No.11を使用したものでは全て軟化、脱落現象が認められたが、これに対し、本発明の酸化防止剤とリン酸系過酸化物分解剤を併用付着せしめた全てのセパレータNo.2〜No.7を使用したものは、セパレータの酸化劣化は全く認められず、而もこれと接触する陽極板の活物質の軟化、脱落も全く認められなかった。特に、サンプルNo.3A、3B、4A、4Bのようにセパレータシートにオイル中に両剤を夫々含有せしめたものを着せしめるときは、過充電寿命８回、SAE寿命3000以上と言う極めて優れた寿命延長効果をもたらすことが判った。

〔発明の効果〕

このように本発明によるセパレータは、酸化防止剤とリン酸系過酸化物分解剤を含有するパラフィン系オイルを付着させた合成樹脂製微多孔性シートから成るので、これを鉛蓄電池に使用するときは、特に、その電池を高温下で使用されてもセパレータの酸化劣化がなく、而も、これと接する陽極板の陽極活物質の軟化、脱落が防止され、高温における鉛蓄電池の充放電サイクル寿命の著しい延長をもたらす等の効果を有する。又、かゝる本発明のセパレータを製造するに当たり、その微多孔性シートの製造後に、酸化防止剤とを含有したパラフィン系オイルを付着させるようにしたので、確実に所望量の酸化防止剤とリン酸系過酸化物分解剤をセパレータの内外面に付着せしめることができる効果をもたらす。

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(54) [Title of the Invention]
SEPARATOR FOR LEAD STORAGE BATTERY AND METHOD OF MANUFACTURING THE SAME

(57) [Patent Claims]

[Claim 1] A separator for a lead storage battery, in which a paraffin oil containing an antioxidant and a phosphoric acid-based peroxide decomposition agent is adhered to the inner and outer surfaces of a microporous sheet made from a synthetic resin.

[Claim 2] The separator for a lead storage battery as described in claim 1, wherein said paraffin oil contains 0.5% or more of the antioxidant and 0.5% or more of the phosphoric acid-based peroxide decomposition agent.

[Claim 3] The separator for a lead storage battery as described in claim 2, wherein the total amount of the antioxidant and the phosphoric acid-based peroxide decomposition agent contained in said paraffin oil is not more than 5%.

[Claim 4] A method of manufacturing a separator for a lead storage battery, in which an inorganic powder and an organic plasticizer are mixed with a polyolefin resin and melt molded into a sheet, all or a portion of the organic plasticizer is then extracted with an organic solvent to form a microporous sheet, and a paraffin oil containing an antioxidant and a phosphoric acid-based peroxide decomposition agent is then adhered to the inner and outer surfaces of the microporous sheet.

[Detailed Description of the Invention]

[Field of the Invention]

The present invention relates to a separator for a lead storage battery and a method of manufacturing the same.

[Prior Art]

Polyethylene separators are well known in the prior art. Such separators are manufactured by mixing a high-density polyethylene resin with an inorganic powder and organic plasticizer; melt molding into a sheet; and then obtaining a microporous structure by extracting all of the organic plasticizers, or a portion thereof, with an organic solvent. Conventional polyethylene separators are thought to have excellent resistance to oxidation.

[Problems Addressed by the Invention]

However, when such polyethylene separators are used in lead storage batteries for electric vehicles or automobiles, the utilization environment of the separators will be severe due to the increased frequency of use and high-temperature utilization conditions in recent years. Under such utilization conditions, the separator will be oxidized and degraded by the oxidation action of oxygen or lead dioxide generated from the positive alloy plate adjacent to the separator, and the intensity of this oxidation action increases with temperature. For this reason, the separator is unexpectedly rapidly oxidized and degraded, and the service life thereof is shortened, in such a severe high temperature utilization environment. On the other hand, the active material of the positive electrode plate of the lead storage battery is easily softened and peels off at such high temperatures, thereby shortening the service life of the battery.

In order to prevent the shortening of service life caused by the oxidation of the separator at high temperatures, which is the above-described drawback in the prior art, the surface of the separator is impregnated with a paraffin oil as a surface protecting agent, but such measure alone fails to provide a sufficient prevention effect with respect to the oxidation-induced degradation.

Furthermore, when an attempt was made to impregnate the separator with a paraffin oil having a phenol-based antioxidant admixed thereto, a certain amount of improvement in the prevention of oxidation-induced degradation of the separator under a high-temperature environment was observed, but the oxidation-induced degradation caused by contact with the positive electrode active material was not prevented, softening and peeling of the positive electrode active material could not be avoided, and shortening of the battery service life was impossible to avoid.

[Means to Resolve the Problems]

The present invention resolves the above-described problems, and provides a separator for a lead storage battery that has increased resistance to oxidation at high temperatures, and is comprised of a function that prevents high-temperature softening and peeling of the positive electrode active material of a lead storage battery. A paraffin oil that contains an antioxidant and a phosphorous acid-based peroxide decomposition agent is adhered to the inner and outer surfaces of a microporous sheet made from a synthetic resin.

Furthermore, the present invention provides a method of manufacturing a separator for a lead storage battery that makes it possible to reliably manufacture a separator for a lead storage battery containing both the antioxidant and the phosphoric acid-based peroxide decomposition agent of the present invention, the method characterized in that an inorganic powder and an organic plasticizer are mixed with a polyolefin resin and melt molded into a sheet, all or a portion of the organic plasticizer is then extracted with an organic solvent to form a microporous sheet, and a paraffin oil containing an

antioxidant and a phosphoric acid-based peroxide decomposition agent is then adhered to the inner and outer surfaces of the microporous sheet.

[Operation]

In the separator for a lead storage battery of the present invention, the inner surfaces of the micropores of the sheet and the outer surfaces of the sheet are covered with a paraffin oil containing an antioxidant and a phosphoric acid-based peroxide decomposition agent. Therefore, inside the battery, the oil itself will prevent the active material of the positive electrode plate, i.e., peroxide, from coming into contact with the separator sheet surfaces. At the same time, the synergetic effect of the antioxidant and phosphoric acid-based peroxide decomposition agent contained in the oil effectively prevents oxidation and chain oxidation of the separator sheet at high temperatures, and also prevents high-temperature oxidation-induced degradation and consumption of the separator sheet. In particular, it effectively prevents softening, that is, the formation of a microporous crystal structure in the positive electrode active material, i.e., lead dioxide, due to the phosphoric acid-based peroxide decomposition agent, and the peeling of the active material resulting therefrom and, therefore, greatly extends the battery service life.

In this case, it is preferred that the antioxidant contained in the paraffin oil be present at 0.5% or more based on the oil, and that the phosphoric acid-based peroxide decomposition agent be present at 0.5% or more based on the oil. It is also particularly preferred that the total amount of the antioxidant and the phosphoric acid-based peroxide decomposition agent contained in the paraffin oil be limited to no more than 5%, such limitation preventing self discharge. In order to manufacture a separator in which an oil containing relatively large amounts of the two components is reliably adhered to the inner and outer surfaces of the microporous sheet, as described in the method of manufacturing above, all or a portion of the organic plasticizer is removed with an organic solvent from a molded sheet to form a microporous sheet, and then a paraffin oil containing the prescribed amounts of the above-described components is adhered to the sheet.

[Embodiments]

An embodiment of the present invention will be described below.

The separator of the present invention is based on a microporous sheet made from a synthetic resin. However, this synthetic resin is preferably a polyolefin resin that is generally considered to have high oxidation resistance, and polyethylene, in particular high-density polyethylene, is preferred because a comparatively hard, thin and strong separator sheet can be obtained. In order to melt mold this resin and obtain a microporous sheet, for example, an inorganic powder resistant to oxidation, such as a finely powdered silicic acid, and an organic plasticizer such as ODP, are mixed at the appropriate ratios with the resin, the blend is heated and melted, and the melt is molded into a sheet by extrusion molding or the like. Then all or a portion of the plasticizer is extruded with any well-known organic solvent to produce a high-density polyethylene sheet having micropores formed therein. The present invention is characterized in that a separator for a lead storage battery is obtained in which a paraffin oil comprising an antioxidant and a phosphorus acid-based peroxide decomposition agent is adhered to the inner surfaces of the pores of the microporous sheet and the outer surfaces of the sheet. However, in the above-described manufacturing method, after the microporous sheet has been fabricated, it can be immersed for a desired amount of time in the paraffin oil containing the above-described two components, or the oil can be uniformly spread in a prescribed amount with a sprayer from the outer surfaces of the sheet, or the oil can be applied with an application roller to impregnate the microporous sheet uniformly therewith. In this case, the separator of the present invention can be manufactured by diluting the paraffin oil containing the two components at the appropriate temperature with the appropriate solvent, impregnating the microporous sheet with the oil, and then drying the solvent at a comparatively low temperature to cause the adhesion of a prescribed quantity of oil.

Furthermore, when the separator of the present invention is assembled into a lead storage battery in accordance with standard methods, the separator will be inserted between the negative electrode and

positive electrode plates to obtain an electrode assembly which is then accommodated in a battery case. As a result, a lead battery can be provided that has oxidation resistance at high temperatures and a long service life, as clearly described hereinbelow.

Note that when the above-described microporous polyethylene sheet is fabricated, in order to prevent thermal oxidation and degradation of polyethylene during heating, melting, and molding, an antioxidant is preferably added to the starting materials. However, this antioxidant is eluted in the process of extracting the plasticizer with an organic solvent, and only traces of the antioxidant are present in the microporous sheet obtained. Therefore, when the microporous sheet is used as the separator for a lead storage battery as is, surface oxidation of the sheet or chain oxidation into the inner parts thereof are unavoidably caused by lead dioxide or oxygen generated from the positive electrode plate, the sheet is oxidized and consumed, the thickness thereof decreases, and oxidation-induced degradation occurs that causes cracking in various places and formation of through holes. As a result, the internal short circuit effect occurs in the lead storage battery, and the battery becomes unsuitable for use. In particular, the oxidation-induced degradation is accelerated, and the service life of the battery is shortened, under utilization conditions such that the temperature inside the battery repeatedly increases. Accordingly, an attempt was made to prevent the separator from oxidation, by adhering a paraffin oil having an antioxidation effect to the separator, or by adhering a paraffin oil comprising only an antioxidant to the separator. As a result, a certain amount of oxidation prevention effect could be obtained. However, the active material of the positive electrode plate was softened and peeled off. Moreover, contact oxidation of the separator unavoidably occurs in this active material, thereby shortening the service life of the battery. In accordance with the present invention, as demonstrated by the results of various research, the combined presence of an antioxidant and a phosphoric acid-based peroxide decomposition agent not only prevents the oxidation of separator even when the lead storage battery is exposed to high temperatures, but also reduces softening and peeling of the active material of the positive electrode plate, thereby extending the service life of the battery, and more specifically, increases the SAE life at high temperatures.

In the present invention, any of the well-known antioxidants can be used, but phenolic antioxidants that cause no damage to the battery, such as 2,2'-methylenebis(4-methyl-6-t-butylphenol), 4,4'-butylidenebis(3-methyl-6-t-butylphenol), and 4,4'-thiobis(3-methyl-6-t-butylphenol), are preferred.

The peroxide decomposition agent used in accordance with the present invention has to be of the phosphoric acid type, such as TNP, because softening and peeling of the active material were found to be impossible to prevent with the peroxide decomposition agents containing no phosphoric acid, such as thiosulfide based peroxide decomposition agents.

Characteristics of the present invention will be clearly described below via comparative testing thereof.

High-density polyethylene (weight-average molecular weight about 200,000) was used as the main component. A fine powder of silicic acid and a paraffin oil as an organic plasticizer were blended at ratios of 100 wt.% and 400 wt.%, respectively, the blend was heated and melted, the mixture was molded into a sheet with a thickness of 0.5 mm with an extrusion molding apparatus, the molded sheet was passed through an organic solvent to extract all or a portion of the organic plasticizer, and then heated and dried to obtain a microporous sheet. Separately, paraffin oils were prepared that contained an antioxidant and a phosphoric acid-based peroxide decomposition agent at different blending ratios, as well as a paraffin oil containing an antioxidant and a peroxide decomposition agent containing no phosphoric acid. Each of the paraffin oils obtained was adhered to the microporous paraffin sheet samples at ratios of 10% and 20%. Furthermore, for comparison, a microporous sheet was also produced in which a paraffin oil alone was adhered to the microporous sheet.

Table 1

Separator sample No.	Content in paraffin oil			Amount of adhered oil (%)
	Antioxidant (%)	Peroxide decomposition agent		
		Based on phosphoric acid (%)	Containing no phosphoric acid (%)	

1	0.1	0.1	-	20
2A	0.5	0.5	-	10
2B	0.5	0.5	-	20
3A	1.0	1.0	-	10
3B	1.0	1.0	-	20
4A	1.0	4.0	-	10
4B	1.0	4.0	-	20
5	2.0	1.0	-	20
6	3.0	1.0	-	20
7	4.0	1.0	-	20
8	5.0	-	-	20
9	-	4.0	-	20
10	-	-	4.0	20
11	1.0	-	4.0	20
12	-	-	-	-

Lead storage batteries for automobiles were prepared by using the separators for lead storage batteries of the above-described samples No. 1 to No. 12, and assembling electrode assemblies by laminating the separators with negative electrode plates and positive electrode plates for lead storage batteries. Then, the tests were conducted to determine the 5-h ratio capacity, C.C.A., overcharge life, and 65° SAE life of the test battery samples No. 1' to No. 12' corresponding to respective separators. The measurement results are shown in Table 2.

Table 2

Lead storage battery sample No.	5-h ratio capacity (Ah)	C.C.A. (A)	Overcharge life (cycles)	65°C SAE life (cycles)
1'	28.5	293	4	2500
2'A	28.5	294	6	2900
2'B	28.5	293	6	3000
3'A	28.5	292	8	3250
3'B	28.3	295	8	3500
4'A	28.3	290	8	3300
4'B	28.5	295	8	3400
5'	28.5	295	6	2950
6'	28.5	294	6	2900
7'	28.5	294	6	2900
8'	28.4	293	5	2550
9'	28.4	294	5	3000
10'	28.5	294	5	2500
11'	28.5	294	6	2500
12'	28.5	294	4	2400

Data shown in Table 1 and Table 2 demonstrate that the test batteries No. 2A' to No. 7' using the separators No. 2A to No. 7 in accordance with the present invention, in which the antioxidant and phosphorus acid-based peroxide decomposition agent were adhered to the separators, demonstrated a significant extension of both the overcharge life and 65°C SAE life in comparison to the batteries using the conventional separators No. 1' and No. 12'. Furthermore, in the battery No. 8 using the separator No. 8 in which an oil comprising only the antioxidant was adhered thereto (comparative test), as shown in Table 2, an extension of the service life of the two types was not observed. Furthermore, in the battery No. 8' using the separator No. 9 in which an oil comprising only the phosphoric acid-based peroxide decomposition agent was adhered thereto, as shown in the same table,

an improvement in SAE life was observed, but practically no extension of overcharge life was observed. Moreover, when the battery was disassembled upon completion of the test and the separator thereof was inspected, the separator was found to have undergone oxidation-induced degradation, the thickness of the sheet decreased, and cracks appeared in various places therein. Furthermore, as shown in the same table, absolutely no extension of SAE life was observed in a battery 11', which respectively used a separator No. 10, to which an oil containing only a peroxide decomposition agent containing no phosphoric acid was adhered, in order to study the effects thereof, and a separator No. 11 to which an oil containing this and an antioxidant was adhered, in order to study the combined effects thereof. Moreover, the oxidation-induced degradation of the separators in the batteries No. 10, No. 10', and No. 11' was found to be similar to that of the sample No. 8 (No. 8').

With respect to all the separator samples and test batteries, softening and peeling of the active material was inspected for the positive electrode plates that came into contact with the separators (the results are not shown in the tables). In all the batteries using the conventional separators No. 1 and No. 12 and also the comparative separators No. 8 to No. 11, softening and peeling were observed. By contrast, in the batteries using the separators No. 2 to No. 7 in accordance with the present invention, in which both the antioxidant and the phosphoric acid-based peroxide decomposition agent were adhered thereto, absolutely no oxidation-induced degradation of the separator was observed, and absolutely no softening and peeling of the active material of the positive electrode plate that is in contact therewith was observed. In particular, when an oil containing both components was adhered to the separator sheet, as in samples No. 3A, 3B, 4A, and 4B, an excellent service life extension effect providing an overcharge life of 8 cycles and a SAE life of 3000 or more was observed.

[Effect of the Invention]

The separator in accordance with the present invention comprises a microporous sheet made from a synthetic resin and having adhered thereto a paraffin oil comprising an antioxidant and a phosphoric acid-based peroxide decomposition agent. Therefore, when this separator is used in a lead storage battery, there will be no oxidation-induced degradation of the separator even when the battery is used at high temperatures. Furthermore, softening and peeling of the positive electrode active material of the positive electrode plate that is in contact with the separator is prevented, and a significant extension of the charge-discharge cycle life of the lead storage battery at high temperatures is attained. Moreover, when the separator of the present invention is manufactured, the paraffin oil containing an antioxidant will be adhered after the microporous sheet has been manufactured. Therefore, the desired amount of antioxidant and phosphoric acid-based peroxide decomposition agent can be reliably adhered to the inner and outer surface of the separator.